PIEZOELECTRIC CERAMIC COMPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a piezoelectric ceramic composition suitable for resonators, filters, sensors and the like.

Description of the Prior Art

Most of the piezoelectric ceramic compositions now being put in practical use are constituted with ferroelectrics having the perovskite structure such as PZT (the $PbZrO_3$-$PbTiO_3$ solid solution) based or PT ($PbTiO_3$) based ferroelectrics having the tetragonal system or the rhombohedral system at around room temperature.

These compositions are substituted with third components such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(Mn_{1/3}Nb_{2/3})O_3$, or various additives are added to these compositions to meet a wide variety of required properties.

The piezoelectric ceramic composition has a capability of freely converting electric energy into mechanical energy or vice versa and extracting the energy, and is used as a resonator, filter, actuator, ignition element, ultrasonic motor or the like. When the piezoelectric ceramic composition is used as a resonator, for example, a high Q_{max} value (Q_{max} = $\tan\theta$: θ is a phase angle) as an electric property is not all that is required. In recent years, surface mount devices have

come into wide use, and high heat resisting properties are also required since the piezoelectric ceramic composition is passed through a solder reflow furnace before it is mounted on a printed board. High or satisfactory heat resisting properties means small dispersions in properties after a thermal shock is given.

For example, Patent Document 1 (Japanese Patent Laid-Open No. 2000-103674) has proposed an improvement of the heat resisting properties of a piezoelectric ceramic composition in which to the main component represented by a general formula $Pb_{\alpha}[(Mn_{1/3}Nb_{2/3})_xTi_yZr_z]O_3$ (in the general formula, $1.00 \leq \alpha \leq 1.05$, $0.07 \leq x \leq 0.28$, $0.42 \leq y \leq 0.62$, and $0.18 \leq z \leq 0.45$, $x + y + z = 1$), Mn_3O_4 is added as an additive from 0.3 to 0.8 wt% in relation to 100 wt% of the main component.

Products having piezoelectric ceramic compositions mounted thereon are used in various environments, and therefore the mechanical strength is one of important properties. It is proposed in, for example, Patent Document 2 (Japanese Patent Laid-Open No. 2003-128462) that SiO_2 is added for improving the flexural strength. However, it is well known that SiO_2 improves the mechanical strength, while it causes a degradation in heat resisting properties, and thus SiO_2 is currently used at some point of compromise between both types of properties.

In Patent Document 1, Mn is incorporated as an additive to improve the heat resisting properties of the piezoelectric ceramic composition and in an example in the document, it is possible to obtain excellent heat resisting properties such that the rate of change in electromechanical coupling factor

k_{15} before and after a heat resistance test is 2.33% as an absolute value. However, a piezoelectric ceramic composition excellent in all of the electric property Q_{max}, heat resisting properties and temperature characteristics of oscillation frequencies has not yet been found in any study including that in Patent Document 1.

SUMMARY OF THE INVENTION

Thus, an object of the present invention is to provide a piezoelectric ceramic composition capable of improving the flexural strength without degrading heat resisting properties. Further, an object of the present invention is to provide a piezoelectric ceramic composition excellent in all of the electric property Q_{max}, heat resisting properties and temperature characteristics of oscillation frequencies.

The present inventors have found that in a piezoelectric ceramic composition of a perovskite structure comprising a lead component, the flexural strength is improved by precipitating an Al-containing phase in relation to a main component comprising lead zirconate titanate (hereinafter may be referred to as PZT). Moreover, the inventors have found that the piezoelectric ceramic composition is improved also for heat resisting properties compared to those with no Al-containing phase. That is, the present invention provides a piezoelectric ceramic composition comprising a phase comprising, as a main component, lead zirconate titanate having a perovskite structure, and an Al-containing phase. For the piezoelectric ceramic composition, it is possible to obtain

heat resisting properties such that the absolute value $|\Delta F_0|$ of the rate of change in oscillation frequency F_0 before and after application of a thermal shock is 0.10% or less, and properties such that the three-point flexural strength σ_{b3} is 160 N/mm^2 or greater.

In the piezoelectric ceramic composition of the present invention, it is preferable that the main component comprises Mn and Nb, and is represented by the composition formula of $Pb_\alpha[(Mn_{1/3}Nb_{2/3})_xTi_yZr_z]O_3$ (wherein $0.97 \leq \alpha \leq 1.01$, $0.04 \leq x \leq 0.16$, $0.48 \leq y \leq 0.58$, $0.32 \leq z \leq 0.41$).

Additionally, in the piezoelectric ceramic composition of the present invention, the Al-containing phase preferably comprises Al_2O_3.

Furthermore, the inventors have found that the above Al is effective for improvement of electric property Q_{max} and temperature characteristics of oscillation frequencies in addition to improvement of heat resisting properties. Moreover, the inventors have found that Ga, In, Ta and Sc exhibit same effects as the effect of Al. That is, the present invention is based on the findings described above, and is a piezoelectric ceramic composition comprising as additives at least one selected from the group consisting of Al, Ga, In, Ta and Sc in an amount of 0.01 to 15.0 wt% in terms of oxides of the elements, in relation to a main component represented by the formula 1, $Pb_\alpha[(Mn_{1/3}Nb_{2/3})_xTi_yZr_z]O_3$, wherein α, x, y and z fall within the ranges of $0.97 \leq \alpha \leq 1.01$, $0.04 \leq x \leq 0.16$, $0.48 \leq y \leq 0.58$ and $0.32 \leq z \leq 0.41$, respectively, and α, x, y and z each represent a molar ratio.

For the piezoelectric ceramic composition of the present invention, it is made possible, by specifying a main component and specifying the elements and amounts of additives, to obtain properties such that the electric property Q_{max} is 30 or greater, the absolute value of the rate of change in electromechanical coupling factor k_{15}, $|\Delta k_{15}|$, before and after application of a thermal shock is 4% or less, the absolute value of the rate of change in oscillation frequency F_0 at -40°C, $|\Delta F_0 (-40°C)|$, with reference to 20°C, is 0.4% or less, and the absolute value of the rate of change in oscillation frequency F_0 at 85°C, $|\Delta F_0 (85°C)|$, with reference to 20°C is 0.4% or less. The properties are specified by methods according to descriptions in the sections of "Detailed Description of the Preferred Embodiments" and "Examples" described later.

It is preferable that the piezoelectric ceramic composition of the present invention has α, x, y and z of the main component falling within the range of $0.98 \le \alpha < 1.00$, $0.06 \le x \le 0.14$, $0.49 \le y \le 0.57$ and $0.33 \le z \le 0.40$, respectively, and comprises Al as an additive in an amount of 0.05 to 5.0 wt% in terms of Al_2O_3. Moreover, the piezoelectric ceramic composition of the present invention preferably comprises Si as an additive in an amount of 0.005 to 0.15 wt% in terms of SiO_2.

According to the present invention described above, a piezoelectric ceramic composition comprising a sintered body having as a main component a perovskite compound having Pb, Zr, Ti, Mn and Nb as main components, and compriseing as additives at least one selected from the group consisting of

Al, Ga, In, Ta and Sc, wherein the electric property Q_{max} is 100 or greater, the absolute value of the rate of change in electromechanical coupling factor k_{15}, $|\Delta k_{15}|$, before and after application of a thermal shock is 2% or less, the absolute value of the rate of change in oscillation frequency F_0 at -40°C, $|\Delta F_0 (-40°C)|$, with reference to 20°C is 0.2% or less, and the absolute value of the rate of change in oscillation frequency F_0 at 85°C, $|\Delta F_0 (85°C)|$, with reference to 20°C is 0.2% or less, can be obtained.

According to the present invention, a piezoelectric ceramic composition having an improved mechanical strength without degradation in heat resisting properties can be obtained by making an Al-containing phase exist in a matrix. Moreover, according to the present invention, a piezoelectric ceramic composition excellent in all of the electric property Q_{max}, heat resisting properties and temperature characteristics of oscillation frequencies can be obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a view for explaining a polarization direction;

FIG. 2 is an equivalent circuit diagram of a piezoelectric resonator;

FIG. 3 is a sectional view of a specimen with vibrating electrodes formed on both upper and lower surfaces;

FIG. 4 is a table showing compositions and properties of specimens of Example 1;

FIG. 5 shows the results of observing element distributions of specimens obtained in Example 1 using the

SEM-EDS (SEM: scanning electron microscope, EDS: energy dispersive spectroscopy) ;

FIG. 6 is a table showing compositions and properties of specimens of Example 2;

FIG. 7 is a table showing compositions and properties of specimens of Example 3; and

FIG. 8 is a table showing compositions and properties of specimens of Example 4.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A piezoelectric ceramic composition according to the present invention will be described in detail below.

<Piezoelectric ceramic Composition>

The piezoelectric ceramic composition according to the present invention has PZT having a perovskite structure as a main component, and the main component preferably comprises Mn and Nb. Further, the piezoelectric ceramic composition according to the present invention has as a main component a perovskite compound having Pb, Zr, Ti, Mn and Nb as main components. The piezoelectric ceramic composition having the above main component according to the present invention is typically composed of a sintered body. The sintered body comprises grains having the above main component and grain boundary phase exists between the grains in addition to a phase having the above main component. In the piezoelectric ceramic composition of present invention, there exists an Al-containing phase in addition to the phase having the above main component, and the Al-containing phase can be generated

by adding a predetermined amount of Al_2O_3 as a raw material. It can be understood that the added Al_2O_3 is randomly precipitated in the sintered body.

As shown in Examples described later, the Al-containing phase is not generated if the amount of Al_2O_3 added is less than a predetermined amount. The effect of improving heat resisting properties can be observed even if the amount of Al_2O_3 added is less than the predetermined amount. In addition, if the amount of Al_2O_3 added is greater than the predetermined amount, both the flexural strength and heat resisting properties are improved. From the results described above, it is estimated that Al_2O_3 is contained in grains (lattices) composed of the main component to exhibit the effect of improving heat resisting properties of the main component, i.e. PZT itself, and excessive Al_2O_3 incapable of being contained in grains is randomly precipitated in mainly grain boundaries of the sintered body to strengthen the binding between grains to contribute to an improvement in flexural strength.

For generating the Al-containing phase exhibiting the effect of improving the flexural strength, Al_2O_3 is added to the main component, especially represented by $Pb_\alpha[(Mn_{1/3}Nb_{2/3})_xTi_yZr_z]O_3$ (formula(1)) in an amount of preferably 0.15 wt% or greater, more preferably 0.6 wt% or greater. The properties of the piezoelectric ceramic composition are not impaired even though the amount of Al_2O_3 added is increased, and therefore the upper limit of the amount is not particularly limited, but since it is understood that

the obtained effect is saturated, the amount of Al_2O_3 added is 15.0 wt% or less, preferably 5.0 wt% or less, further preferably 1.5 wt% or less in relation to the main component.

The piezoelectric ceramic composition of the present invention preferably has a main component represented by the following formula (1). The chemical composition mentioned herein is a composition after sintering.

$Pb_\alpha[(Mn_{1/3}Nb_{2/3})_xTi_yZr_z]O_3$ ...formula (1)

wherein α, x, y and z fall within the ranges of $0.97 \leq \alpha \leq 1.01$, $0.04 \leq x \leq 0.16$, $0.48 \leq y \leq 0.58$ and $0.32 \leq z \leq 0.41$, respectively, and α, x, y and z each represent a molar ratio.

Next, description will be made below on the reasons for imposing constraints on α, x, y and z in formula (1).

The quantity α representing the Pb content is constrained to fall within the range of $0.97 \leq \alpha \leq 1.01$. When α is less than 0.97, it is difficult to obtain a dense sintered body. On the other hand, when α exceeds 1.01, no satisfactory heat resisting properties can be obtained. Accordingly, α is constrained to fall within the range of $0.97 \leq \alpha \leq 1.01$. The range of α is preferably $0.98 \leq \alpha < 1.00$, and more preferably $0.99 \leq \alpha < 1.00$.

The quantity x determining the Mn content and the Nb content is constrained to fall within the range of $0.04 \leq x \leq 0.16$.

If x is less than 0.04, the electric property Q_{max} is small. On the other hand, when x exceeds 0.16, no satisfactory heat resisting properties can be obtained. Accordingly, x is constrained to fall within the range of $0.04 \leq x \leq 0.16$. The

range of x is preferably $0.06 \leq x \leq 0.14$, and more preferably $0.07 \leq x \leq 0.11$.

The quantity y representing the Ti content is constrained to fall within the range of $0.48 \leq y \leq 0.58$. When y is less than 0.48, no satisfactory heat resisting properties can be obtained. On the other hand, when y exceeds 0.58, it is difficult to obtain satisfactory temperature characteristics. Accordingly, y is constrained to fall within the range of $0.48 \leq y \leq 0.58$. The range of y is preferably $0.49 \leq y \leq 0.57$, and more preferably $0.50 \leq y \leq 0.55$.

Satisfactory temperature characteristics means small dispersions in properties of the piezoelectric ceramic composition associated with a change in temperature in working environments.

The quantity z representing the Zr content is constrained to fall within the range of $0.32 \leq z \leq 0.41$. When z is less than 0.32, or exceeds 0.41, no satisfactory temperature characteristics can be obtained. Accordingly, z is constrained to fall within the range of $0.32 \leq z \leq 0.41$. The range of z is preferably $0.33 \leq z \leq 0.40$, and more preferably $0.34 \leq z \leq 0.39$.

The piezoelectric ceramic composition having the above main component according to the present invention may comprise as additives at least one element selected from the group consisting of Ga, In, Ta and Sc in an amount of 0.01 to 15.0 wt% in terms of the oxide of each element, in addition to Al described above. Incorporation of the above additives into the above main component provides a piezoelectric ceramic

composition excellent in electric property, heat resisting properties and temperature characteristics. The amount of additive is 0.01 to 15.0 wt%, preferably 0.05 to 5.0 wt%, further preferably 0.15 to 1.5 wt% in terms of the oxide of the element in relation to $Pb_{\alpha}[(Mn_{1/3}Nb_{2/3})_xTi_yZr_z]O_3$ of the formula (1). Al is most preferably used as an additive.

In addition, SiO_2 may be incorporated as an additive to the piezoelectric ceramic composition according to the present invention. The incorporation of SiO_2 is effective for improving the flexural strength of piezoelectric ceramic composition. When SiO_2 is incorporated, in relation to $Pb_{\alpha}[(Mn_{1/3}Nb_{2/3})_xTi_yZr_z]O_3$ in formula (1), the SiO_2 content is preferably 0.005 to 0.15 wt%, more preferably 0.01 to 0.12 wt%, and further preferably 0.01 to 0.07 wt%.

<Production Method>

Now, description will be made below on the preferable production method of the piezoelectric ceramic composition according to the present invention, by following the sequence of the steps of the method.

(Raw Material Powders and Weighing Out)

As the raw materials for the main components, there are used powders of oxides or powders of compounds to be converted to oxides when heated. More specifically, PbO powder, TiO_2 powder, ZrO_2 powder, $MnCO_3$ powder, Nb_2O_5 powder and the like can be used. The raw material powders are weighed out respectively so that the composition represented by formula (1) may be actualized.

Then, oxide powders of at least one element selected from the group consisting of Al, Ga, In, Ta and Sc are added as additives in an amount of 0.01 to 15.0 wt% in relation to the total weight of the component powders. As raw material powders of additives, Al_2O_3 powder, Ga_2O_3 powder, Ta_2O_5 powder, Sc_2O_3 powder and In_2O_3 powder may be used.

When SiO_2 is to be incorporated in addition to these additives, additionally SiO_2 powder is prepared. It is recommended that the mean particle size of each of the raw material powders is appropriately selected within the range of 0.1 to 3.0 μm.

Incidentally, without restricting to the above described raw material powders, a powder of a composite oxide containing two or more metals may be used as a raw material powder.

(Calcination)

The raw material powders are subjected to wet mixing and then subjected to a calcination while being maintained at temperatures falling within the range from 700 to 950°C for a predetermined period of time. This calcination is recommended to be conducted under the atmosphere of N_2 or air, setting the maintaining time within the range from 0.5 to 5.0 hours.

Incidentally, although description has been made above for the case where the powders of the main components and the additives are mixed together, and then both of them are subjected to calcination, the timing for adding the raw material of the additives is not limited to the above described timing. Alternatively, for example, firstly the powders of

the main components are weighed out, mixed, calcined and pulverized; then, to the main component powder thus obtained after calcination and pulverization, the raw material powder of the additives may be added in a predetermined content to be mixed with the main component powder.

(Granulation and Compacting)

The pulverized powder is granulated for the purpose of smoothly carrying out a subsequent compacting step.

At this time, a small amount of an appropriate binder, for example polyvinyl alcohol (PVA) is added to the pulverized powder, and they are sufficiently mixed, and granulated through, for example, a mesh to obtain a granulated powder.

Then, the thus granulated powder is compacted by pressing under a pressure of 200 to 300 MPa to obtain a compacted body having a desired shape.

(Sintering)

After the binder, added at the time of molding, has been removed from the compacted body, the compacted body is heated and maintained at temperatures within the range from 1100 to 1250°C for a predetermined period of time to obtain a sintered body. In this connection, the atmosphere is recommended to be N_2 or air. The maintaining time period of the heating is recommended to be appropriately selected within the range from 0.5 to 4 hours.

(Polarization)

After electrodes for the polarization have been formed on the sintered body, the polarization is carried out. The polarization is conducted under the conditions such that the

polarization temperature falls within the range from 50 to 300°C, and an electric field of 1.0 to 2.0 Ec (Ec being the coercive field) is applied to the sintered body for 0.5 to 30 minutes.

When the polarization temperature is lower than 50°C, the Ec is elevated and accordingly the voltage needed for polarization becomes high, so that the polarization is made difficult. On the other hand, when the polarization temperature exceeds 300°C, the insulation property of the insulating oil is markedly lowered, so that the polarization is made difficult. Consequently, the polarization temperature is made to fall within the range from 50 to 300°C. The polarization temperature is preferably 60 to 250°C, and more preferably 80 to 200°C.

Additionally, when the applied electric field is lower than 1.0 Ec, the polarization does not proceed. On the other hand, when the applied electric field is higher than 2.0 Ec, the actual voltage becomes high, so that the dielectric breakdown of sintered body tends to be occurred and accordingly it becomes difficult to prepare a piezoelectric ceramic composition. Accordingly, the electric filed to be applied in the polarization is made to be 1.0 to 2.0 Ec. The applied electric field is preferably 1.1 to 1.8 Ec, and more preferably 1.2 to 1.6 Ec.

When the polarization time is less than 0.5 minute, the polarization is not progressed to a sufficient extent, so that the properties cannot be attained to a sufficient extent. On the other hand, when the polarization time exceeds 30 minutes,

the time required for the polarization becomes long, so that the production efficiency is degraded. Accordingly, the polarization time is made to be 0.5 to 30 minutes. The polarization time is preferably 0.7 to 20 minutes, and more preferably 0.9 to 15 minutes.

The polarization is conducted in a bath of an insulating oil such as a silicon oil heated to the above described temperature. Incidentally, the polarization direction is determined according to the desired vibrational mode. In this connection, when the desired vibrational mode is a thickness-shear vibration mode, the polarization direction is taken as shown in FIG. 1A; the thickness-shear vibration is such a vibration as illustrated in FIG. 1B.

The piezoelectric ceramic composition is lapped to a desired thickness, and thereafter vibrating electrodes are formed. Then, using a dicing saw or the like, the piezoelectric ceramic composition is cut into a desired shape to function as a piezoelectric element.

The piezoelectric ceramic composition of the present invention is suitably used as the materials for the piezoelectric elements for use in resonators, filters, actuators, ignition elements, ultrasonic motors and the like.

<Properties of Piezoelectric ceramic composition>

(Flexural Strength)

For the piezoelectric ceramic composition of the present invention, it is possible to obtain a mechanical strength such that the three-point flexural strength σ_{b3} is 160 N/mm^2 or

greater, preferably 170 N/mm^2 or greater, further preferably 180 N/mm^2 or greater.

Here, the three-point flexural strength σ_{b3} in the present invention is determined from the following formula (2) in accordance with Japanese Industrial Standards JIS R 1601. In the formula (2), P represents a load (N), L represents a distance (m) between support rolls, w represents a width (m) of a specimen, t represents a thickness (m) of a specimen, and yb represents a net displacement (m) at a load point.

$$\sigma_{b3} = \frac{L^3(P_2 - P_1)}{4wt^3(y_{b2} - y_{b1})} \quad \text{... formula (2)}$$

(Heat Resisting Properties)

The piezoelectric ceramic composition of the present invention can have excellent heat resisting properties. In the present invention, heat resisting properties were evaluated on two criteria. One is a heat resisting property regarding an oscillation frequency F_0, and the other is a heat resisting property regarding an electromechanical coupling factor k_{15}. They will be described below in this order.

For the piezoelectric ceramic composition of the present invention, the heat resisting property $|\Delta F_0|$ regarding the oscillation frequency F_0 can be 0.10% or less. The heat resisting property $|\Delta F_0|$ is determined as follows. The ΔF_0 of the obtained specimen is measured (before test), and the specimen is then wrapped with an aluminum foil, and immersed in a solder bath at 265°C for 10 seconds. Then, the specimen is taken out from the aluminum foil, and left standing in air

at room temperature for 24 hours. After the specimen is left standing for 24 hours, ΔF_0 is measured again (after test). The rate of change in F_0 before and after the test (after 24 hours) is determined based on the formula (3), and heat resisting properties are evaluated by the absolute value ($|\Delta F_0|$). $|\Delta F_0|$ is the absolute value of the rate of change in oscillation frequency F_0 before and after application of a thermal shock. $|\Delta F_0|$ obtained in the Example described later is determined by the same procedure.

$$\Delta F_0 = \frac{F_0(\text{after test}) - F_0(\text{before test})}{F_0(\text{after test})} \times 100(\%) \qquad \ldots \text{ formula (3)}$$

The oscillation frequency F_0 in the present invention is related to the following formulas (4) to (7) in terms of the equivalent circuit constants.

In formulas (4) to (7), F_0 represents an oscillation frequency, Fr represents a resonant frequency, Fa represents an anti-resonant frequency, C_1 represents a motional capacitance, C_0 represents a shunt capacitance, C_L is defined in the formula (7), Cd represents a free capacitance, and C_{L1} and C_{L2} each represent a load capacitance. An equivalent circuit for the piezoelectric resonator is shown in FIG. 2. In FIG. 2, R_0 represents a resonant impedance, L_1 represents an equivalent inductance, C_1 represents a motional capacitance, and C_0 represents the shunt capacitance.

As shown by formula (4), the oscillation frequency F_0 is dependent on the four parameters, namely, the resonant frequency Fr, the motional capacitance C_1, the shunt capacitance C_0, and C_L. Additionally, as shown by formulas

(5) to (7), the motional capacitance C_1, the shunt capacitance C_0, and C_L each are associated with plural parameters.

$$F_0 = Fr\sqrt{1+\frac{C_1}{C_0+C_L}} \quad \text{... formula (4)}$$

$$C_1 = \frac{Fa^2 - Fr^2}{Fa^2} Cd \quad \text{... formula (5)}$$

$$C_0 = Cd - C_1 \quad \text{... formula (6)}$$

$$C_L = \frac{C_{L1} \cdot C_{L2}}{C_{L1} + C_{L2}} \Rightarrow \frac{C_{L1}}{2}(C_{L1} = C_{L2}) \quad \text{... formula (7)}$$

For the piezoelectric ceramic composition of the present invention, the heat resisting property $|\Delta k_{15}|$ regarding the electromechanical coupling factor k_{15} can be 4% or less. The heat resisting property $|\Delta k_{15}|$ in the present invention is obtained on the basis of the following procedures. The electromechanical coupling factor k_{15} is measured with a measurement frequency of about 4 MHz by use of an impedance analyzer (4294A manufactured by Agilent Technologies Co., Ltd.). The electromechanical coupling factor k_{15} is obtained on the basis of the following formula (8).

In the formula (8), Fr represents a resonant frequency, and Fa represents an anti-resonant frequency. The

electromechanical coupling factor k_{15} of the obtained specimen is measured (before test), and the specimen is then wrapped with an aluminum foil, and immersed in a solder bath at 265°C for 10 seconds. Then, the specimen is taken out from the aluminum foil, and left standing in air at room temperature for 24 hours. After the specimen is left standing for 24 hours, the electromechanical coupling factor k_{15} is measured again. The rate of change in Δk_{15} before and after the test (after 24 hours) is determined based on the formula (9), and heat resisting properties are evaluated by the absolute value ($|\Delta k_{15}|$). $|\Delta k_{15}|$ is the absolute value of the rate of change in electromechanical coupling factor k_{15} before and after application of a thermal shock. $|\Delta k_{15}|$ obtained in the Examples described later is determined by the same procedure.

$$k_{15} = \sqrt{\frac{\pi}{2} \frac{Fr}{Fa} \cot \left(\frac{\pi}{2} \frac{Fr}{Fa} \right)} \quad \text{... formula (8)}$$

$$\Delta k_{15} = \frac{k_{15}(\text{after test}) - k_{15}(\text{before test})}{k_{15}(\text{after test})} \times 100(\%) \quad \text{... formula (9)}$$

(Electric Property Q_{max})

For the piezoelectric ceramic composition of the present invention, it is possible to obtain electric properties such that Q_{max} is 30 or greater, preferably 80 or greater, further preferably 100 or greater. Q_{max} represents a maximum value of Q (= tan θ, θ: phase angle (deg)) between the resonant frequency fr and the anti-resonant frequency fa, is one of important properties as a resonator, and contributes to low-voltage drive.

The piezoelectric ceramic composition is also excellent in temperature characteristics. For the present invention, the temperature property regarding the oscillation frequency can be 0.4% or less. For this temperature property, an oscillation frequency F_0 (20°C) at 20°C is measured as a reference, and further an oscillation frequency (-40°C) at -40°C and an oscillation frequency (85°C) at 85°C are measured. The rate of change in oscillation frequency, ΔF_0(-40°C), between the oscillation frequency F_0 and the oscillation frequency (-40°C) at -40°C, and the rate of change in oscillation frequency, ΔF_0(85°C), between the oscillation frequency F_0 and the oscillation frequency (85°C) at 85°C are determined from formulas (10) and (11) to evaluate temperature characteristics.

$$\Delta F_0(-40℃) = \frac{F_0(-40℃) - F_0(20℃)}{F_0(20℃)} \times 100(\%)$$

... formula (10)

$$\Delta F_0(85℃) = \frac{F_0(85℃) - F_0(20℃)}{F_0(20℃)} \times 100(\%)$$

... formula (11)

For the piezoelectric ceramic composition of the present invention, it is possible to obtain electric properties such that Q_{max} is 30 or greater, heat resisting properties such that $|\Delta k_{15}|$ is 4% or less, and temperature characteristics such that $|\Delta F_0$ (-40°C)$|$ is 0.4% or less and $|\Delta F_0$ (85°C)$|$ is 0.4% or less.

Further, according to the present invention, it is possible to obtain electric properties such that Q_{max} is 100

or greater, heat resisting properties such that $|\Delta k_{15}|$ is 2% or less, and temperature characteristics such that $|\Delta F_0$ (-40°C)$|$ is 0.2% or less and $|\Delta F_0$ (85°C)$|$ is 0.2% or less.

Further, according to the present invention, it is possible to obtain electric properties such that Q_{max} is 120 or greater, heat resisting properties such that $|\Delta k_{15}|$ is 1.8% or less, and temperature characteristics such that $|\Delta F_0$ (-40°C)$|$ is 0.1% or less and $|\Delta F_0$ (85°C)$|$ is 0.1% or less.

[Example 1]

As the raw materials, there were prepared the powders of PbO, TiO_2, ZrO_2, $MnCO_3$, Nb_2O_5, Al_2O_3 and SiO_2; the raw material powders were weighed out in such a way that the formula, $Pb_{0.99}[(Mn_{1/3}Nb_{2/3})_{0.10}Ti_{0.53}Zr_{0.37}]O_3$ in molar ratio was satisfied. Thereafter, SiO_2 as an additive was added in an amount of 0.02 wt% in relation to the total weight of the powders, Al_2O_3 powder was added in the amount shown in FIG. 4, and they were wet-mixed for 10 hours using a ball mill.

The slurries thus obtained were dried to a sufficient level, and compacted with a press, thereafter calcined in air in a manner maintained at 800°C for 2 hours. The calcined substances were pulverizied with a ball mill so as to have a mean particle size of 0.7 μm, and then the pulverized powders were dried. The dried powders were added with PVA (polyvinyl alcohol) as a binder in an appropriate content, and were granulated. About 3 g of the granulated powder was put into a die having a 20 mm long × 20 mm wide cavity, and the granulated powder was compacted under a pressure of 245 MPa using a uniaxial press machine. The compacted bodies thus obtained were

subjected to the treatment for removing the binder, and thereafter maintained at 1150 to 1250°C for 2 hours in the air to obtain sintered bodies (specimens) each having the size of 17.5 mm long × 17.5 mm wide × 1.5 mm thick.

Both surfaces of the specimen were flattened by a lapping machine to obtain a thickness of 0.5 mm, the specimen was then cut into a size of 15 mm long × 5.0 mm wide, and temporary electrodes for polarization were formed at both ends thereof (along the width of 5.0 mm). Thereafter, the specimens each were subjected to a polarization in which each of the specimens was immersed in a silicon oil bath at 150°C, and applied an electric field of 3.0 kV/mm for 15 minute. Here, it should be noted that the polarization direction was chosen as shown in FIG. 1A. Subsequently, the temporary electrodes for polarization were removed. Here, it should also be noted that the size of each of the specimens after removing the temporary electrodes was 15 mm long × 4 mm wide × 0.5 mm thick. Both surfaces of each of the specimens were lapped by a lapping machine so as for the thickness of each of the specimens to be 0.3 mm, and then, vibrating electrodes 2 were formed on both surfaces (both polished surfaces) of each of the specimens 1 with the aid of a vacuum evaporation apparatus, as shown in FIG. 3. The vibrating electrodes 2 were each formed of a 0.01 μm thick Cr sublayer and a 2 μm thick Ag layer. The overlapping area of each of the vibrating electrodes 2 was made to be 1.5 mm long along the lengthwise direction.

Subsequently, from each of the above described specimens 1, a 4 mm long × 0.7 mm wide × 0.3 mm thick piezoelectric element

was cut out. In this way, a specimen for measurement of the electric property Q_{max} was obtained (FIG. 3). The results of measurement of the electric property Q_{max} are shown in FIG. 4. The electric property Q_{max} was measured at around 4 MHz using an impedance analyzer (4294A manufactured by Agilent Technology Co., Ltd.). Q_{max} represents a maximum value of Q (= tan θ, θ: phase angle (deg)) between the resonant frequency fr and the anti-resonant frequency fa, which is one of important properties as a resonator and contributes to low-voltage drive.

For the mechanical strength, both surfaces of the above specimen were flattened by the lapping machine to obtain a thickness of 0.32 mm, the specimen was then cut into a size of 7.2 mm long × 2.5 mm wide using a dicing saw, and the three-point flexural strength σ_{b3} was determined from the formula (2) with a strength tester (Model 5543) manufactured by INSTRON Co, Ltd. The results are shown in FIG. 4.

Additionally, using the specimen for which Q_{max} had been measured, $|\Delta F_0|$ was determined by the procedure described above. The results are shown in FIG. 4.

Additionally, the surface to be observed of the above specimen was polished with a diamond paste, and the element distribution thereof was observed by the EDS (energy dispersive spectroscopy) of an SEM (scanning electron microscope). The results are shown in FIG. 5. FIG. 5 shows that white areas have high concentrations of Al, and existence or nonexistence of the Al-containing phase was determined based on the result of this measurement. The results are shown in FIG. 4. In FIG. 4, a cross (×) indicates that the Al-containing phase

does not exist, and an open circle (○) indicates that Al-containing phase exists. The Al-containing phase has a size of approximately 0.5 to 10 μm.

As shown in FIG. 4, it can be understood that existence of the Al-containing phase improves the heat resisting properties, and also improves Q_{max} and the flexural strength. Addition of 0.1 wt% of Al_2O_3 does not result in generation of the Al-containing phase. Thus, it is understood that Al_2O_3 is contained in grains (lattices) composed of the main component to contribute to an improvement in heat resisting properties. Excessive Al_2O_3 incapable of being contained in grains is randomly precipitated in the grain boundaries to strengthen the binding between grains to contribute to an improvement in flexural strength. Thus, it is preferable that the amount of Al_2O_3 is set so that the Al-containing phase is formed in the piezoelectric ceramic composition if the flexural strength is required. By doing so, it is made possible to obtain a three-point flexural strength σ_{b3} of 160 N/mm^2 or greater, further 170 N/mm^2 or greater, and still further 190 N/mm^2 or greater.

[Example 2]

A raw material powder same as that of Example 1 was weighed so as to obtain a composition of $Pb_{0.998}[(Mn_{1/3}Nb_{2/3})_{0.10}Ti_{0.51}Zr_{0.39}]O_3$ or $Pb_{0.990}[(Mn_{1/3}Nb_{2/3})_{0.10}Ti_{0.53}Zr_{0.37}]O_3$ in molar ratio, SiO_2 as an additive was then added in an amount of 0.02 wt% in relation to the total weight of the powders, Al_2O_3 powder was added

in the amount shown in FIG. 6, and they were wet-mixed for 10 hours using a ball mill.

Specimens for measurement of the electric property Q_{max} and the electromechanical coupling factor k_{15} were obtained in the same manner as in Example 1 (FIG. 3). The electromechanical coupling factor k_{15} represents efficiency of conversion from electric energy into mechanical energy or vice versa in a thickness-shear vibration mode, which is one of basic properties of a piezoelectric material, and it was calculated from the formula (7). For measurement of the electric property Q_{max} and the electromechanical coupling factor k_{15}, the impedance analyzer (4294A manufactured by Agilent Technology Co., Ltd.) was used.

The obtained electric properties Q_{max} are shown in FIG. 6. Using the specimen for which the electric property Q_{max} had been measured, $|\Delta k_{15}|$ was determined by the procedure described above. The results are shown in FIG. 6.

The specimen, for which the electric property Q_{max} had been measured, was placed in a thermostatic bath at 20°C, and the oscillation frequency F_0 (20°C) at 20°C was measured by a frequency counter (53181A manufactured by Agilent Technology Co., Ltd.) when the temperature was sufficiently stabilized. The specimen, for which the oscillation frequency F_0 (20°C) at 20°C had been measured, was placed in thermostatic baths at -40°C and 85°C, and oscillation frequencies F_0 (-40°C) and F_0 (85°C) were measured when the temperature was sufficiently stabilized. Using the results of this measurement, $|\Delta F_0$ (-40°C)$|$ and $|\Delta F_0$ (85°C)$|$ were calculated from the formulas (10)

and (11). The results of the measurement described above are shown in FIG. 6.

As shown in FIG. 6, the heat resisting property (the absolute value of the rate of change in electromechanical coupling factor k_{15}: $|\Delta k_{15}|$) is improved as the amount of Al_2O_3 added as an additive is increased. High levels of electric properties, heat resisting properties and temperature characteristics can be ensured even if the amount of Al_2O_3 added exceeds 10 wt%, although they depend on the composition of the main component. Thus, in the present invention, the amount of Al_2O_3 added is 0.01 to 15.0 wt%. If the amount of Al_2O_3 added is in this range, temperature characteristics of $|\Delta F_0\ (-40°C)| \leq 0.4\%$ and $|\Delta F_0\ (85°C)| \leq 0.4\%$ can be obtained.

[Example 3]

The powder was weighed so as to obtain the composition shown in FIG. 7 (main component: $Pb_\alpha[(Mn_{1/3}Nb_{2/3})_xTi_yZr_z]O_3$), a piezoelectric ceramic composition was then fabricated in the same manner as in Example 2, and the properties were measured in the same manner as in Example 2. The results are shown in FIG. 7. In Example 3, Al_2O_3 and SiO_2 as additives are fixed, while values of α, x, y and z in the main component are varied. The marks, *, given to the specimen Nos. in FIG. 7 indicate Comparative Examples.

When specimens for which α representing the Pb content is 0.990 (Nos. 29 to 32) are compared with specimens for which α is 0.995 (Nos. 45 to 48), it can be said that they are comparable in temperature characteristics, but specimens for which α is

0.995 are superior in both electric properties Q_{max} and heat resisting properties.

The specimen for which x representing the contents of Mn and Nb are small, i.e. 0.02 (No. 20), has a low value of the electric property Q_{max}, i.e. less than 30. Higher x is more preferable for the electric property Q_{max}, but tends to degrade heat resisting properties.

For the specimen having a large content of Ti, for which y is 0.59 (No. 27), the absolute value of ΔF_0 (85°C), $|\Delta F_0$ (85°C)$|$, which is one of parameters of temperature characteristics, exceeds 0.4%. Referring to specimens No. 33 to 37, it can be understood that the temperature characteristcs $|\Delta F_0$ (85°C)$|$ tends to be degraded as y decreases.

Additionally, for specimens having a large content of Zr, for which z is 0.42 (Nos. 24 and 26), temperature characteristics are degraded. However, temperature characteristics tend to be degraded as z, i.e. the Zr content, decreases.

In the present invention, based on the above results, the main component has a composition in which α, x, y and z fall respectively within the ranges of $0.97 \le \alpha \le 1.01$, $0.04 \le x \le 0.16$, $0.48 \le y \le 0.58$ and $0.32 \le z \le 0.41$ in $Pb_{\alpha}[(Mn_{1/3}Nb_{2/3})_xTi_yZr_z]O_3$ (formula(1)).

[Example 4]

A piezoelectric ceramic composition having the composition shown in FIG. 8 was fabricated in the same manner as in Example 2, and the properties were measured in the same manner as in Example 2. The results are shown in FIG. 8. Ga_2O_3

powder, Ta_2O_3 powder, Sc_2O_3 powder and In_2O_3 powder were prepared as raw material powders.

As shown in FIG. 8, it has been found that Ga_2O_3, Ta_2O_3, Sc_2O_3 and In_2O_3 exhibit effects same as those of Al_2O_3 described in Examples 1 and 2.